Investigating a Drop-on-Demand Microdispenser for Standardized Sample Preparation

by Ellen L. Holthoff, Mikella E. Farrell, and Paul M. Pellegrino

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Adelphi, MD 20783-1197

Investigating a Drop-on-Demand Microdispenser for Standardized Sample Preparation

Ellen L. Holthoff, Mikella E. Farrell, and Paul M. Pellegrino
Sensors and Electron Devices Directorate, ARL

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
September 2012	Reprint	

4. TITLE AND SUBTITLE

Investigating a Drop-on-Demand Microdispenser for Standardized Sample Preparation

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Ellen L. Holthoff, Mikella E. Farrell, and Paul M. Pellegrino

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Research Laboratory
ATTN: RDRL-SEE-E
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-RP-0396

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

A reprint from the *Proc. of SPIE,* Vol. 8358, 83580V-1.

14. ABSTRACT

The existing assortment of reference sample preparation methods presents a range of variability and reproducibility concerns, making it increasingly difficult to assess chemical detection technologies on a level playing field. We are investigating a drop-on-demand table-top printing platform which allows precise liquid sample deposition and is well suited for the preparation of uniform and reproducible reference materials. Current research focuses the development of a sample preparation protocol for explosive materials testing based on drop-on-demand technology. Device settings were determined for optimal droplet formation and velocity. Droplet mass and reproducibility were measured using ultraviolet-visible (UV-Vis) absorption and a sensitive microbalance. The results presented here demonstrate the operational factors that influence droplet dispensing for specific materials (e.g. energetic and interferents). Understanding these parameters allows for the determination of droplet and sample uniformity and reproducibility (typical calibration goodness of fit R^2 values of 0.991, relative standard deviation or RSD $\leq 5\%$), and thus the demonstrated development of a successful and robust methodology for energetic sample preparation.

15. SUBJECT TERMS

Microdrop, drop-on-demand, inkjet printer

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	UU	14	Mikella Farrell
Unclassified	Unclassified	Unclassified			**19b. TELEPHONE NUMBER** *(Include area code)* (301) 394-0948

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Investigating a Drop-on-Demand Microdispenser for Standardized Sample Preparation

Ellen L. Holthoff*, Mikella E. Farrell, Paul M. Pellegrino

U.S. Army Research Laboratory, RDRL-SEE-E, 2800 Powder Mill Road, Adelphi, MD, 20783

ABSTRACT

The existing assortment of reference sample preparation methods presents a range of variability and reproducibility concerns, making it increasingly difficult to assess chemical detection technologies on a level playing field. We are investigating a drop-on-demand table-top printing platform which allows precise liquid sample deposition and is well suited for the preparation of uniform and reproducible reference materials. Current research focuses the development of a sample preparation protocol for explosive materials testing based on drop-on-demand technology. Device settings were determined for optimal droplet formation and velocity. Droplet mass and reproducibility were measured using ultraviolet-visible (UV-Vis) absorption and a sensitive microbalance. The results presented here demonstrate the operational factors that influence droplet dispensing for specific materials (e.g. energetic and interferents). Understanding these parameters allows for the determination of droplet and sample uniformity and reproducibility (typical calibration goodness of fit R^2 values of 0.991, relative standard deviation or RSD $\leq 5\%$), and thus the demonstrated development of a successful and robust methodology for energetic sample preparation.

Keywords: Microdrop, drop-on-demand, inkjet printer

1. INTRODUCTION

The detection and identification of trace explosive residues on surfaces is a priority for the military and homeland defense applications, and first responders. Technology evaluation of systems based on optical detection techniques that allow for ranged sensing is complicated by spatial dependencies and a lack of a reliable means to generate calibrated reference samples containing the explosive materials. Reference materials and methods are needed to establish benchmarks for hazard detection system development, verification of system performance in the field, and technology comparisons between systems. Furthermore, an assortment of explosive reference materials are needed to allow for flexibility to react to the diverse and ever-changing range of threats encountered.[8] A variety of techniques that offer temporary alternatives have been employed, including drop-and-dry (dropcasting) and spray deposition methods; however, it is often observed that there is uneven sample coverage (i.e., coffee ring effect) and material waste. Using drop-on-demand inkjet printing technology to produce test materials is an attractive approach to meet the requirements for sample standardization. Unlike other sample preparation methods that often result in the "coffee ring" effect, for which most of the material is concentrated along the edges, samples prepared using drop-on-demand inkjet technology have an excellent uniform material dispersion throughout. A visual comparison of these sample preparation methods and the uniformity achieved with each can be easily demonstrated with SEM images and photographs, see Figure 1.[2, 3]

Piezoelectric drop-on-demand inkjet printing is an efficient approach for the non-contact deposition of microdroplets of solutions onto a surface.[5] This technique is compatible with various liquids, providing precise control over material deposition. Additionally, a range of deposited material concentrations can be achieved by varying the number and spacing of microdrops printed. As a non-contact printing process, the inkjet fluid cannot be contaminated by the substrate or contamination on the substrate, and the fluid can be easily dispensed into wells or other substrate features.[6] Drop-on-demand technology has been successfully used in a variety of applications, including the printing of photodiodes, polymer and protein arrays, and in electronics manufacturing.[7, 9, 12, 13] These applications benefit from the wide range of liquids that can be dosed, the small volumes handled, the accuracy of drop placement, and the quantitative volume delivery. The reproducibility of optimized drop-on-demand systems has been reported to be better than 1% relative standard deviation (RSD) from measurement-to-measurement (within-day) and better than 2% RSD for day-to-

day measurements of dispensed volumes.[1, 11] These errors are significantly lower than those observed for other sample preparation methods.
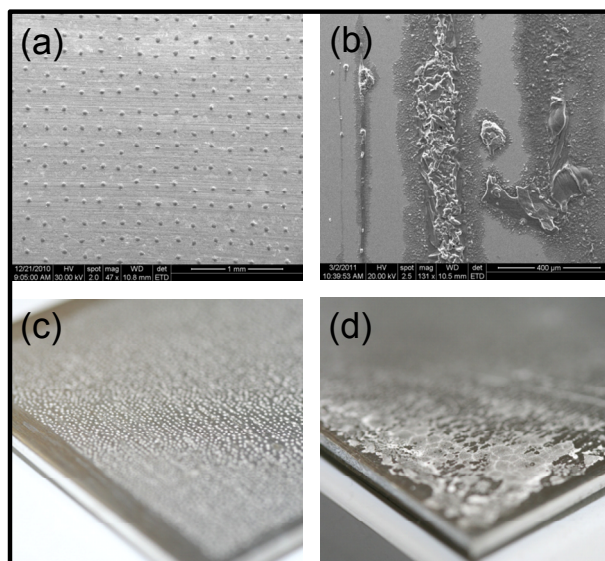

Figure 1. SEM images of representative samples (at different magnifications) prepared using the (a) JetLab[®] 4 drop-on-demand inkjet printer and (b) drop and dry method. Images (c) and (d) are photographs of these samples, respectively.

Recently, we have utilized a commercial off-the-shelf (COTS) drop-on-demand printing platform for the preparation of a variety of samples to be used in field tests for the assessment of the hazard detection capability of an optical detection system. Here, we report the development and proven feasibility of this sample preparation method to produce both energetic and interferent test materials. Microdrop mass was determined and validated using two different techniques, (1) a microbalance and (2) an ultraviolet-visible (UV-Vis) spectrophotometer. These measurements allowed for simple and inexpensive system calibrations to verify the mass of various target materials deposited with each microdrop.

2. EXPERIMENTAL

2.1 Reagents and Materials

Target Analyte Stock Solutions. Ammonium nitrate (AN), methanol (MeOH), distilled water (H$_2$O), acetonitrile, sugar, urea, and potassium chlorate were obtained from Sigma-Aldrich. 1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN) were obtained from Cerilliant. All inkjet printer stock solutions were prepared in a solution of methanol (MeOH) and water (v/v 2:1), acetonitrile, or water, depending on solubility. All stock solutions were sonicated for 30 min prior to use to ensure homogeneity.

All chemicals were used as received unless otherwise noted.

2.2 Inkjet Printing

Test materials were produced using a JetLab[®] 4 (MicroFab Technologies) tabletop printing platform. The system is shown in Figure 2(a). The JetLab[®] 4 is a drop-on-demand inkjet printing system with drop ejection drive electronics (JetDrive[TM] III), pressure controller, a drop visualization system, and precision *X*, *Y*, *Z* motion control. The dispensing device (print head assembly, MJ-AL-01-060) consists of a glass capillary tube, with a 60 µm diameter orifice coupled to a piezoelectric element. Photographs of the dispensing device encasement and the print head assembly are shown in Figures 2(b) and 2(c), respectively. Voltage pulses (20–25 V; rise time 1 µs; dwell time 28–32 µs; fall time 1 µs) applied to the piezo result in pressure fluctuations around the capillary. These pressure oscillations propagate through the printing fluid in the tube, resulting in ejection of a microdrop.
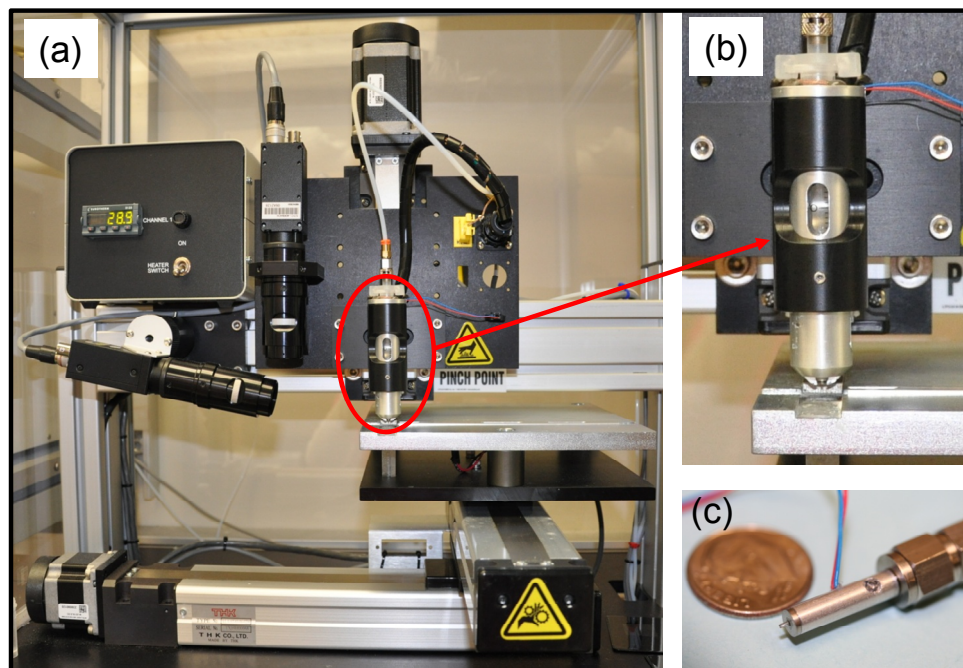
Figure 2. Photographs of (a) JetLab® 4 drop-on-demand inkjet printing platform; (b) dispensing device and ink solution encasement; and (c) print head assembly.

Determining optimal jetting parameters is a trial-and-error process. Stable droplet ejection is achieved by visually observing expelled microdrops and adjusting voltage pulse parameters and capillary fluid backfill pressure to create an "ideal" drop. Drops are visualized using synchronized strobe illumination and a charged coupled device (CCD) camera (Figure 3). Conditions that provide the highest drop velocity without satellite droplet formation are desired. Printing was performed at a frequency of 250 Hz with a droplet velocity of ~2 m/s. Drop diameter was estimated to be ~60 µm, based on the capillary orifice diameter. For clarification, the dwell time is the time during which the piezo wave form changes shape when a drive voltage is applied to the piezoelectric device for a given amount of time. An optimal drop is a droplet typically equal in size to the dispensing orifice being used, which does not have satellites, and consistently falls at an optimum velocity. Satellites are secondary droplets, following the optimal droplet, typically observed to be smaller in volume than the optimal droplet. Satellites deposited add to a total concentration error and can affect droplet spacing uniformity.
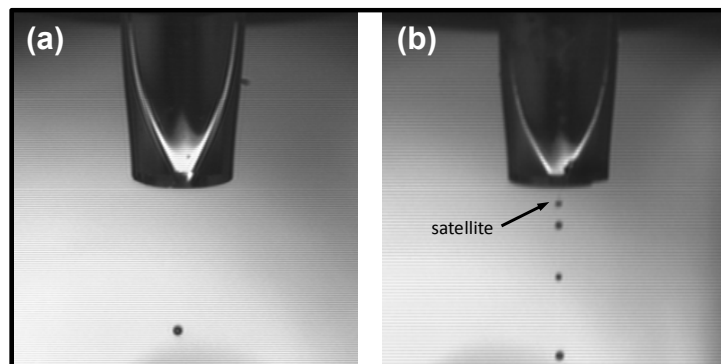

Figure 3. Drop generation from JetLab® 4 drop-on-demand inkjet printer. Stable droplet ejection (a) is achieved by adjusting voltage and pressure parameters. Satellite drop formation (b) is not desired and can often be eliminated by decreasing the voltage.

During printing, a single vessel was placed on the sample stage. The print head remained fixed at a specified height while the stage moved to print a specified pattern or number of microdrops. A rectangular area, which covers an area with rows and columns of equidistant points, was pre-programmed based on the vessel size. The total number of drops needed to achieve a desired concentration per unit area is calculated based on the volume of a single microdrop and the solution concentration. Based on the number of total drops needed, the array spacing and drops needed per line can be calculated. These values are easily adjusted depending on solution concentration. Patterns were printed using the print on-the-fly mode. In this mode, the stage moves continuously as a single microdrop is dispensed at each array element. Print on-the-fly mode improves sample throughput. For multiple droplets deposited at a single point, burst mode was used.

2.3 UV-Vis Absorption Spectroscopy

UV-Vis absorption spectroscopy measurements were collected using a Shimadzu® UV-3600 UV-VIS spectrophotometer. Calibration curves were constructed by measuring standard solutions (of known sample concentrations) containing various pre-determined energetic and interferent compounds. The evaluated analytes were: AN, potassium chlorate, HMX, TNT, RDX, PETN, urea, and sugar. The analyte of interest was dissolved in the appropriate solvent and then diluted to various concentrations. Absorbance was measured using quartz cuvettes (1 cm path length) in a dual beam UV-Vis. One cuvette was filled with 3 mL of analyte solution (sample), and the other was filled with 3 mL of pure solvent (blank, H_2O or acetonitrile). Wavelength scans from 190–400 nm were used to measure the absorbance of the various target materials at known concentrations. The analytes of interest had absorption features in this wavelength region.[2]

2.4 Gravimetry

Droplet mass was measured using a Mettler-Toledo XP2U microbalance. A known number of microdroplets were dispensed (burst mode) onto a (pre-weighed) weighing vessel placed on the inkjet printer sample stage. Following droplet ejection, the solvent was allowed to evaporate, leaving only material residue. The weighing vessel was then removed from the printer and placed on the pan of the microbalance to record the mass. In some instances, the vessel was placed back on the sample stage of the printer and droplets were again dispensed. This cycle was repeated at least 8 times. Additional sampling methods included depositing the same number of microdrops onto at least 3 different weighing vessels and weighing each vessel individually to determine variability. For each method, the calculated mass changes for the total number of droplets deposited were used for single droplet mass determinations.

3. RESULTS AND DISCUSSION

We report microdroplet optimization results for a dispensing device having a 60 µm orifice with analyte samples in conjunction with acetonitrile, MeOH:H_2O, and H_2O solvents. We also discuss the performance for the microdrop mass calibration methods described, as applied to selected inkjet stock solutions. This includes the repeatability and standard uncertainties of the measurements. Potential biases arising from variations in operational conditions are considered.

3.1 Microdroplet Optimization Results

Prior to analyte deposition onto a substrate surface, it was important to completely understand the drop-on-demand instrument settings, and the influence of the dispensing device orifice size and the inkjet printing solvent used. Many variables can impact the drop; therefore, optimized parameters are needed to achieve the best drop at a sufficient velocity. *Controlling the physical properties (e.g., size, volume) of the dispensed microdrops and the ability to do so is very important, as these parameters will ultimately affect droplet variation and reproducibility.* Desired drop velocity is between 1 and 2 m/s. In all cases, it was found that in order to maintain a consistent drop with a suitable velocity, several variables needed to be changed, including the dwell time and voltage applied to the dispensing device.

Using a 60 µm diameter dispensing device, acetonitrile proved to be a challenging solvent for obtaining and maintaining an optimal drop. The parameters shown in Table 1 were uniquely capable of producing a good satellite-free drop. In order to maintain a consistent drop, the dwell time needed to be set between 31 and 34 µs. As the dwell time was

increased, the voltage could be set between 17 and 22 V. We found that by increasing the dwell time and voltage, the velocity of the drop increased (shown in Figure 4(a)). While maintaining a consistent drop, the velocity did not change at voltages greater than 18 V. The highest velocity found was 1.11 m/s.

Solvent	Tip Size (µm)	Dwell Time (µs)	Voltage (V)	Velocity (m/s)
Acetonitrile	60	31	17	0.888
		34	19	1.110
MeOH:H$_2$O	60	28	20	1.110
		28	21	1.332
		30	23	1.554
		31	28	1.998

Table 1. Parameters for an optimal drop using acetonitrile and a 2:1 MeOH:H$_2$O ratio solution with a 60 µm dispensing device orifice.
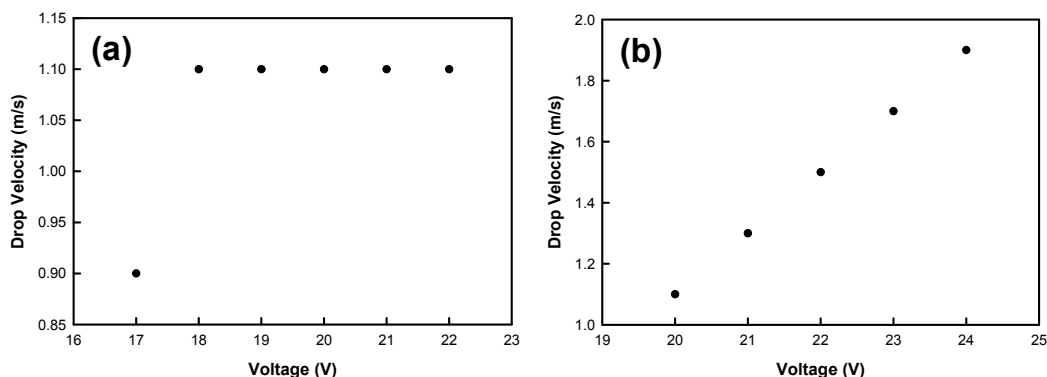

Figure 4. Using a 60 µm dispensing device, changes in drop velocity at different voltages for (a) acetonitrile and (b) 2:1 MeOH:H$_2$O ratio solution are shown.

When a 60 µm tip was used, the MeOH:H$_2$O solution proved to be an easy solvent with which to work, because many settings could be used to obtain a good drop (parameters shown in Table 1). In order to maintain a consistent drop, the dwell time needed to be set between 28 and 31 µs. With the dwell time set within those limits, the voltage could be set between 20 and 28 V. It was found that by maintaining the same dwell time but increasing the voltage, the velocity of the drop increased (shown in Figure 4(b)). Increasing the voltage above 24 V resulted in a loss of drop consistency. Therefore, setting the dwell time and velocity at 31 µs and 24 V, respectively, gives the best drop with the optimum velocity.

3.2 Microdroplet Mass Determination

UV-Vis Absorbance Spectroscopy. To determine the microdroplet mass for each material of interest, a calibration curve was constructed using known concentrations of analytes and absorbance spectral peak areas (shown in Figure 5(a)). Calibration curves were used to prepare linear regressions from which the microdroplet mass and standard error could be calculated using the equation of the line and goodness of fit value (R^2 value). The equation of the line was of the form y = mx + b, where y is the peak area, m is the slope, x is the concentration, and b is the y intercept. Example absorbance spectra and the corresponding calibration curves for AN, TNT, and HMX are shown in Figure 5(b), (c), and (d), respectively.

By determining the mass of material dispensed per droplet, test materials containing a range of sample concentrations were successfully produced. The mass per drop of each analyte of interest was determined by dispensing known numbers of drops into a Petri dish containing a known amount of solvent. Spectral peak areas for these droplets in

solution were determined from the UV-Vis absorbance spectra. These y values were then substituted into the respective calibration curve equation ($y = mx + b$) to determine solution concentration. This methodology was repeated at least three times and resulted in excellent typical RSD values of 5%.
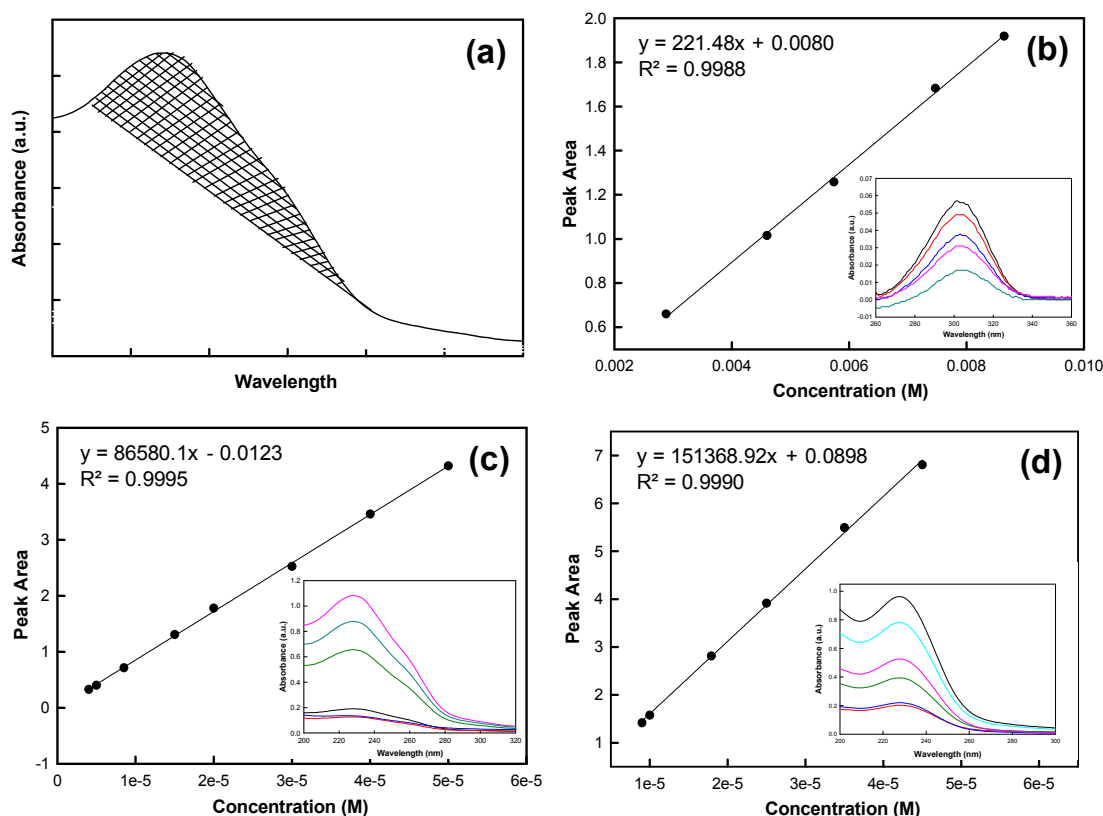

Figure 5. (a) Example absorbance spectrum illustrating peak area used to construct UV-Vis calibration curves. (b) AN calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations. (c) TNT calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations. (d) HMX calibration curve and R^2 value from one UV-Vis data set at various analyte concentrations.

Microbalance Mass Measurements. The mass of material per drop was determined by dispensing a known number of drops onto a weighing vessel (glass slide) and using a sensitive microbalance for gravimetric analysis. Gravimetric data collected for multiple AN deposition cycles are shown in Table 2, note the differences in the mass between each measurement. Each measurement was collected following the deposition of 2000 drops onto the weighing vessel. For this gravimetric method, a precision of 20% RSD for the determination of droplet mass was achieved. This is based on eleven 2000-drop burst cycles. Solvent properties and evaporation rates, as well as AN interaction with water in the surrounding atmosphere (humidity) may have contributed to the increased RSD.

Variability in the burst method is related to the number of drops per burst. The first 10 ejected drops are different in diameter, and therefore mass, from subsequent drops. Improved RSD values for larger aliquots (bursts having >1000 drops) have been reported.[10] With this in mind, gravimetric data was collected for AN following two 5000-drop bursts onto four separate vessels. Not only was a larger aliquot of AN inkjet solution used, but samples were also dried in an oven at 30 ºC for one hour before the mass was recorded in order to minimize humidity affects. Gravimetric data collected for this method of AN deposition is given in Table 3. In this case, the differences in the four separate mass measurements are minimal and an excellent precision of <2% RSD for the determination of droplet mass was achieved.

Measured Mass (µg) 2000 drops	Δ Mass (µg) 2000 drops	Δ Mass (µg) 1 drop
258909.1	initial	initial
258919.4	10.3	5.2E-03
258934.1	14.7	7.4E-03
258951.1	17.0	8.5E-03
258960.8	9.7	4.9E-03
258973.2	12.4	6.2E-03
258983.0	9.8	4.9E-03
258992.2	9.2	4.6E-03
259006.5	14.3	7.2E-03
259019.0	12.5	6.3E-03
259030.6	11.6	5.8E-03
259041.8	11.2	5.6E-03

Table 2. Gravimetric data for AN inkjet solution deposited over 11 cycles, with one 2000-drop burst deposited per cycle.

Vessel #	Initial Mass (µg)	Final Mass (µg) 10000 drops	Δ Mass (µg) 10000 drops	Δ Mass (µg) 1 drop
1	255680.0	255753.1	73.1	7.3E-03
2	254216.8	254291.3	74.5	7.5E-03
3	258909.6	258984.7	75.1	7.5E-03
4	260682.2	260754.6	72.4	7.2E-03

Table 3. Gravimetric data for AN inkjet solution deposited in two 5000-drop bursts.

Comparisons. The preparation of standardized samples requires a microdroplet mass calibration method(s) to ensure sample reproducibility and uniformity. Although spectroscopy techniques offer a simple and viable calibration method, no single standalone technique is appropriate for the plethora of chemical hazards that exist. For example, UV-Vis absorbance spectroscopy, which worked well for the majority of analytes of interest discussed here, may prove difficult for some materials that do not exhibit strong absorbance features in the wavelength range of the instrument. The use of a gravimetric method, such as a quartz crystal microbalance[4] (QCM) or a sensitive microbalance as discussed in this report, is a practical alternative, as excellent precision in the determination of droplet mass can be achieved using appropriate experimental considerations.

4. CONCLUSION

We have investigated a sample preparation protocol that produces uniform samples to be used for utility assessments of emerging optical detection technologies. We considered two methods for determining the mass of droplets ejected from a drop-on-demand inkjet printer that allow for system calibration and the preparation of specific sample material mass loadings. Optimization of microdroplet formation provides microdispensing with specific drop placement and pattern printing capabilities. Continued improvements to use of the inkjet system and sample preparation procedures will further decrease RSD values for the microdrop samples. Based on these findings, we can confidently conclude that using a COTS drop-on-demand system in combination with our analysis and validation techniques is ideal for the fabrication of reference energetic and interferent test materials, and should be considered a predominant and universal innovative industry standard.

REFERENCES

[1]   M. Englmann, A. Fekete, I. Gebefugi, and P. Schmitt-Kopplin, "The dosage of small volumes for chromatographic quantifications using a drop-on-demand dispenser system," Anal. Bioanal. Chem. 388, 1109 (2007).

[2]   E. Holthoff, M. Hankus, K. Tober, and P. Pellegrino, "Investigating a drop-on-demand microdispenser for standardized sample preparation," ARL-TR-5726 (2011).

[3]   E. L. Holthoff, M. E. Hankus, and P. M. Pellegrino, "Investigating a drop-on-demand microdispenser for standardized sample preparation," Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XII 8018, 80181F (2011).

[4]   E. L. Holthoff, M. E. Hankus, and P. M. Pellegrino, "Investigating a drop-on-demand microdispenser for standardized sample preparation," Proc. SPIE - Int. Soc. Opt. Eng. 8018, 80181F (2011).

[5]   E. R. Lee, [Microdrop Generation (Nano- and Microscience, Engineering, Technology and Medicine)] CRC Press, Boca Raton, FL (2003).

[6]   I. MicroFab Technologies, "Background on inkjet technology", in *Technical Notes No. 99-01* (Plano, TX, 1999).

[7]   J. Miettinen, K. Kaija, M. Mantysalo, P. Mansikkamaki, M. Kuchiki, M. Tsubouchi, R. Ronkka, K. Hashizume, and A. Kamigori, "Molded Substrates for Inkjet Printed Modules," IEEE Transactions on Components and Packaging Technologies 32, 2, 293 (2009).

[8]   J. C. Oxley, "Non-traditional explosives: Potential detection problems," Terrorism and Political Violence 5, 2, 30 (1993).

[9]   B. K. Singh and A. C. Hillier, "Multicolor surface plasmon resonance imaging of ink jet-printed protein microarrays," Analytical Chemistry 79, 14, 5124 (2007).

[10]   R. M. Verkouteren and J. R. Verkouteren, "Inkjet Metrology: High-Accuracy Mass Measurements of Microdroplets Produced by a Drop-on-Demand Dispenser," Analytical Chemistry 81, 20, 8577 (2009).

[11]   E. Windsor, M. Najarro, A. Bloom, B. Benner, R. Fletcher, R. Lareau, and G. Gillen, "Application of inkjet printing technology to produce test materials of 1,3,5-trinitro-1,3,5-triazcyclohexane for trace explosive analysis," Anal. Chem. 82, 8519 (2010).

[12]   J. Xia, D. Qu, H. N. Yang, J. J. Chen, and W. L. Zhu, "Self assembly polymer microlens array for integral imaging," Displays 31, 4-5, 186 (2010).

[13] Y. Yang, S. Omi, R. Goto, M. Yahiro, M. Era, H. Watanabe, and Y. Oki, "Wavelength sensitive photodiodes in the visible based on J-type aggregated films patterned by inkjet method," Organic Electronics 12, 3, 405 (2010).

NO. OF
COPIES   ORGANIZATION

    1   ADMNSTR
             DEFNS TECHL INFO CTR
             ATTN DTIC OCP
             8725 JOHN J KINGMAN RD STE 0944
             FT BELVOIR VA 22060-6218

    8   US ARMY RSRCH LAB
             ATTN IMAL HRA MAIL & RECORDS MGMT
             ATTN RDRL CIO LL TECHL LIB
             ATTN RDRL CIO LT TECHL PUB
             ATTN RDRL SEE E M FARRELL (5 HCS)
             ADELPHI MD 20783-1197

INTENTIONALLY LEFT BLANK.